From Pseudo to True $C_3$ Symmetry: Magnetic Anisotropy Enhanced by Site-Specific Ligand Substitution in Two Mn$_{15}$-Carboxylate Clusters

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Two new mixed-valence manganese–carboxylate clusters, [Mn$^{III}_{9}$Mn$^{IV}_{6}$(O$_2$CPh)$_{12}$(μ$_{2}$-O)$_{13}$(μ-O)$_{4}$(μ-OMe)$_{5}$(MeOH)$_{6}$](PhCO$_2$H)$_2$-1.5PhCO$_2$H-MeOH+6H$_2$O (1, PhCO$_2$H = benzoic acid) and [Mn$^{III}_{9}$Mn$^{IV}_{6}$(O$_2$CC$_6$H$_5$)$_{12}$(μ$_{2}$-O)$_{13}$(μ-O)$_{4}$(μ-OMe)$_{5}$](MeOH)$_3$[H$_2$O]$_6$-0.5MeOH-2H$_2$O (2, ChCO$_2$H = cyclohexanecarboxylic acid) contain new disklike Mn$_{15}$ cores. Both 1 and 2 can be synthesized by the conventional manganese redox reaction (MnO$_2$ → oxidizing Mn$^{III}$) in methanol solution. 2 can be also synthesized via the site-specific ligand substitution reaction from 1. 1 crystallizes in the triclinic space group $P\overline{1}$, whereas 2 crystallizes in the trigonal space group $R\overline{3}$. Magnetic study shows that both 1 and 2 have the same ground spin states $S_T = 2$. Compared to the silence of the out-of-phase ac susceptibility of 1, 2 shows clearly slow magnetic relaxation behavior above 1.8 K due to the dramatically enhanced axial magnetic anisotropy ($D = -0.89$ and $-1.58$ cm$^{-1}$ for 1 and 2, respectively, which was obtained by fitting the plots of $M$ vs $H/T$ with the program ANISOFIT 2.0).

1. Introduction

The research for single-molecule magnets (SMMs) with a higher blocking temperature has accelerated the synthetic efforts aimed at the structural control of cluster architecture with large ground-spin states ($S_T$) and axial zero-field splitting parameters ($D_m$). The increase of $S_T$ is obviously based on ferromagnetic interactions between the spins, whereas the enhancement of the $D_m$ is mainly associated with the magnetic anisotropy of the cluster, which in turn depends on the local anisotropies of the single ions and their vectorial addition to give a resulting anisotropy. Because the $D_m$ tensor is mainly determined by the projection of a single-site zero-field-splitting parameter ($D_h$) onto $S_T$, $D_m$ may vanish when the metal–ion arrangement approaches a cubic symmetry. Moreover, quantum tunneling magnetization (QTM) is related to the second-order transverse magnetic anisotropy ($E_m$), which is exactly zero for molecules with strictly axial symmetry. Thus, the control of molecular topology is critical in tuning molecules with large energy barriers and controlling QTM mechanisms.

After understanding the origin of magnetic anisotropy, a lot of synthetic effort has been paid to prepare or modify molecules in a controlled fashion. An elegant strategy is based on the site-specific modification of preformed cluster architectures, which was first introduced in studying the chemical environments on the magnetic properties of the famous Mn$_{12}$ clusters by substituting a variety of outer-

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Zheng et al.

2. Experimental Section

General Remarks. All of the chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elemental Vario-EL CHNS elemental analyzer. FTIR spectra were recorded from KBr pellets in the range 4000–400 cm−1 on a Bio-Rad FT-S 7 spectrometer.

Synthesis. Preparation of 1. To a methanol solution (30 mL) of benzoic acid (0.61 g, 5 mmol), MnCl2·4H2O (0.198 g, 1.0 mmol) and KMnO4 (0.079 g 0.5 mmol) were added with magnetic stirring. The solution then turned black, and the beaker was sealed with a Parafilm for a further ca. 24 h of stirring. After filtration, the filtrate was allowed to stand at room temperature. After two weeks, black plate-like crystals of 1 were collected and washed with acetone (30–40% yield based on Mn). IR data for 1 (KBr, cm−1): 3380 m, 1703 m, 1596 vs, 1558 s, 713 s, 670 s, 648 s, 613 s, 551 m, 522 m. Anal. Calcd for 1: C, 38.45; H, 3.71; Found: C, 38.49; H, 3.65.

Preparation of 2. 2 can be prepared in a similar way to 1 except that cyclohexanecarboxylic acid was used instead of benzoic acid. 2 can be also prepared from 1, that is 1 (0.308 g, 0.05 mmol) was dissolved in MeOH/EtO (1:4 v/v, 40 mL) and treated with cyclohexanecarboxylic acid (0.128 g, 1.0 mmol). After 12 h of stirring, the black solution becomes homogeneous. Black prismatic crystals of 2 were obtained after one week (60–70% yield based on Mn). IR data for 2 (KBr, cm−1): 3425 m, 2955 m, 2853 m, 1601 vs, 1548 s, 1444 s, 1410 s, 1040 m, 930 m, 856 m, 763 w, 700–612 m, 525 m, 448 w. Anal. Calcd for 2: C, 36.52; H, 5.90; Found: C, 36.59; H, 5.82.

X-ray Study. Diffraction intensities of 1 and 2 were collected on a Bruker Apex CCD area-detector diffractometer (Mo Kα, λ = 0.71073 Å). Absorption corrections were applied by using multisiscan program SADABS. The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package. All anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å) as well as the aqua hydrogen atoms (O–H 0.85 Å). Data collection parameters

(10) G. M. Sheldick, SADABS 2.05, University Göttingen: Göttingen, Germany.
From Pseudo to True $C_3$ Symmetry

Table 1. Crystallographic Data and Structural Refinements for 1 and 2

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<th>compound</th>
<th>1</th>
<th>2</th>
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<td>2</td>
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<td>0.0589</td>
</tr>
<tr>
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<td>0.1720</td>
</tr>
<tr>
<td>Residues (e Å$^{-3}$)</td>
<td>1.327 and $-0.795$</td>
<td>0.792 and $-0.456$</td>
</tr>
</tbody>
</table>

$^a$ $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{1/2}$.

Scheme 1 Ligand Substitution Reaction

$[\text{Mn}^\text{III}_n \text{Mn}^\text{IV}_n (\text{O}_3 \text{CPh})_2 \text{Ph}_{2} \text{O}_{2} \text{O}_{2} \text{Mn}^\text{IV}_g \text{MeOH}_g (\text{H}_2 \text{O})_3 + 12 \text{CH}_3 \text{CO}_2 \text{H} + \text{H}_2 \text{O} \rightarrow$

$^1$ $[\text{Mn}^\text{III}_n \text{Mn}^\text{IV}_n (\text{O}_3 \text{CPh})_2 \text{Ph}_{2} \text{O}_{2} \text{O}_{2} \text{Mn}^\text{IV}_g \text{MeOH}_g (\text{H}_2 \text{O})_3 + 12 \text{Ph}_3 \text{CO}_2 \text{H} + \text{MeOH} (1)$

and structure solution details are listed in Table 1. Selected bond distances and angles are listed in Tables S1 and S2.

Magnetic Study. Magnetic susceptibility measurements of 1 and 2 were performed with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples of 1 and 2 were embedded in vanadyl to prevent torquing. All of the ac susceptibility data were collected at zero dc field and 5 Oe ac amplitude. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

3. Results and Discussion

Synthesis. The unprecedented Mn$_{15}$ core was synthesized via a conventional manganese redox reaction (MnO$_2$ oxidizing Mn$^{2+}$) in a benzoic acid–methanol solution. The formation of 1 and 2 rather than other previously reported manganese species may be attributed to the long period of vigorous stirring, which also produces a lot of unknown black precipitate. Therefore, the yield of 1 is not so high (30–40%). To eliminate the intermolecular $\sigma-\pi$ stacking interactions, which we considered as the biggest hindrance in observing the slow-magnetic relaxation behavior in 1 (below), we attempted to replace the benzoate with an analogous $\alpha$-bonded and stronger cyclohexanecarboxylate that can efficiently separate the intercluster magnetic interactions. Fortunately, the replacement led to the formation of 2 (Scheme 1) in high yield, which presents the first site-specific ligand substitution taking place on the manganese cluster with a nuclearity greater than 12, although such substitution has long been succeeded in the Mn$_{12}$ clusters.

Crystal Structures. Single-crystal structures of 1 and 2 feature similar disklike Mn$_{15}$ clusters (Figure 1), formulated as $[\text{Mn}^\text{III}_n \text{Mn}^\text{IV}_n (\text{O}_3 \text{CPh})_2 (\text{Ph}_2 \text{O})_2 (\text{Ph}_3 \text{O})_2 (\text{MeOH}) (\text{HOR})_2] (R_1 = \text{phenyl} or \text{cyclohexane}, R_2 = \text{H or Me})$. Each Mn$_{15}$ core contains six coplanar Mn$^{IV}$ ions in the bottom, nine noncoplanar Mn$^{III}$ ions at the edges, 13 $\mu$-O$^{-2}$ ions as the bridges between Mn$^{III}$ and Mn$^{IV}$ ions, and 12 carboxylates on the outer shell. In addition, the Mn$^{III}$ and Mn$^{IV}$ ions are also bridged by disordered $\mu$-O$^{-2}$– $\mu$-OMe groups (Scheme 2a). The disordered $\mu$-O$^{-2}$– $\mu$-OMe groups have a total ratio of 5:4, according to the charge–balance requirement and elemental analysis. This conclusion is also supported by Bond Valence Sum (BVS) calculations (Table S3) on these disordered oxygen positions, which give values in range of 1.32(2) to 1.54(1), significantly larger than 1.0 for a normal monovalence $\mu$-OMe group, yet smaller than 2.0 for a normal divalent $\mu$-O$^{-2}$– group. A similar situation was observed in some other manganese-based SMMs.

The overall structure of the Mn$_{15}$ core has significant similarity to that of Mn$_{12}$.

Both the Mn$_{12}$ and Mn$_{15}$ cores comprise a nonplanar Mn$^{IV}$ ring around a central Mn$^{IV}$ unit, except that the central Mn$^{IV}$ ions of Mn$_{15}$ are coplanar and quite below the ring Mn$^{III}$, whereas the central Mn$^{IV}$ ions of Mn$_{12}$ are in a cube and almost coplanar with the ring Mn$^{III}$ units. The members of this family now include Mn$_{12}$ ($x = 8, y = 4$), Mn$_{15}$ ($x = 9, y = 6$), Mn$_{16}$ ($x = 10, y = 6$), and Mn$_{21}$ ($x = 12, y = 9$).

Nevertheless, the difference between the Mn$_{15}$ cores in 1 and 2 is also evident from the structural parameters. The cluster in 1 contains only C$_3$ symmetry, although it bears a pseudo-C$_3$ axis (defined as perpendicular to the plane comprising the six Mn$^{IV}$ ions) passing through the central $\mu_2$-O$^{2-}$ ion. In contrast, the cluster in 2 contains a crystal-
Meanwhile all of the Mn III ions are in elongated octahedra and H2O ligands (Scheme 2b) on the Mn15 cores are also more compact than that in 1. In contrast to the small geometric differences in the Mn15 cores, the crystal packing differences in 1 and 2 are more pronounced. The orientations (Figures 2a and S1) of the disclike Mn15 cores in 1 are somewhat intricate due to the low crystallographic symmetry. Each pair of the Mn15 molecules in 1 is only inversely related, having significant intercluster π−π stacking interactions between the phenyl rings with the short distances of 3.38 Å for face-to-face and

\[ \text{Mn}^{III} \]

\[ \text{Mn}^{IV} \]

\[ \text{O} \]

\[ \text{Ph} \]

\[ \text{OH}_2 \]

\[ \text{C} \]

\[ \text{O} \]

\[ \text{MeOH} \]

\[ \text{H}_2 \text{O} \]

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\[ \text{O} \]

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\[ \text{C} \]

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\[ \text{MeOH} \]

\[ \text{H}_2 \text{O} \]

\[ \text{C} \]

\[ \text{OH}_2 \]

\[ \text{O} \]

\[ \text{Ph} \]

\[ \text{C} \]

\[ \text{O} \]

\[ \text{MeOH} \]

\[ \text{H}_2 \text{O} \]

\[ \text{C} \]

\[ \text{OH}_2 \]
3.48 Å for edge-to-face π–π stacking. The shortest intercluster Mn⋯Mn distance is 7.380 Å in 1. As shown in Figures 2b and S2, the disklike Mn_{15} cores in 2 are all orderly arranged around the c axis with the disk bottom pointing alternately up and down in relation to the I₃ symmetry, featuring no strong intercluster interaction other than van der Waals forces. The shortest intermolecular Mn⋯Mn distance is 7.579 Å in 2, being slightly longer than that in 1.

Interestingly, the packing of the Mn_{15} molecules in 2 leaves a channel with an effect diameter of ca. 3.77 Å along the c axis to accommodate the solvent molecules that cannot be totally determined by X-ray single-crystal diffraction.

**Magnetic Properties.** The structural effects on the magnetic properties of 1 and 2 are very interesting. The dc susceptibility data under an applied field of 1000 Oe (Figure 3) show that the χT values at 300 K are 28.46 and 25.49 cm³ mol⁻¹ K per Mn_{15} molecule for 1 and 2, respectively. Both of the values are much smaller than the expected spin-only value of 38.21 cm³ mol⁻¹ K for a noninteracting Mn_{3}Mn_{6} unit, indicating a dominant antiferromagnetic coupling between the metal centers. This phenomenon is very common in some antiferromagnetic manganese clusters. The smaller χT value for 2 is probably due to the more compact arrangement of the Mn_{15} core that leads to stronger antiferromagnetic interactions. Upon cooling, the χT values gradually decrease to 2.97 and 3.03 cm³ mol⁻¹ K at 2 K for 1 and 2, respectively. These values correspond very well to S = 2 and g = 2. Moreover, the χT values from 10 to 2 K are virtually identical to the χ′ values from the temperature-dependent in-phase (χ″) alternating current (ac) magnetic susceptibility (Figure S3), confirming that both 1 and 2 have the same ground spin state S = 2. This method is regarded as the most reliable way to determine the ground states of molecules with low-lying excited states even at the low temperature employed. S = 2 corresponds very well to a spin-coupling scheme in which all of the manganese centers are antiferromagnetically coupled, leading to only one Mn_{III} spin retained for the odd number of the total Mn_{III} spins (for details, see Scheme S1). For such a small S, we can hardly expect the presence of SMMs behavior for 1 or 2. This is the exactly case for 1. However, a clearly frequency-dependent out-of-phase signal is observed for 2 (Figure 4). This surprising behavior is a very positive signal for the SMMs behavior although it does not mean all, because spin-glass or random-domain magnets can also lead to such signals. To further investigate this behavior, isothermal frequency-dependent ac susceptibility data were collected to evaluate the effective energy barrier for 2 (Figure 5). The data were fitted by a generalized Debye model (for details, see Eqs S1 and S2, and Figure S4). The obtained τ values from χ″ are further used and fitted by the Arrhenius law [τ = τ₀exp(U_{eff}/k_B T)], giving U_{eff} = 8.9(1) K.


and \( t_0 = 5.25 \times 10^{-7} \) s. Magnetization data were also collected in a dc magnetic field and in temperature ranges of 0.1–7.0 T and 1.8–4.0 K, respectively, and were fitted by the program ANISOFIT 2.0.\(^{17}\) However, attempts to fit the data above 3 T were unsuccessful, which suggests that possible low-lying excited states are still populated. This presumption is consistent with the isothermal field-dependent magnetization at 1.8 K (Figure 6), in which the maximum value of 1 and 2 reaches 5.32\( \mu_B \) and 4.95\( \mu_B \) at 7 T, respectively. These values are significantly larger than 4\( \mu_B \), as expected for the \( S_T = 2 \) (assuming \( g = 2 \)) ground states, unambiguously indicating the existence of the low-lying excited states even at the operating limit of our SQUID. However, it does not affect 2 to behave as an SMM. The best fits were carried by using the low-field data (0.1–2.0 T), which is also regarded as the reliable way in determining the ground states of molecules with low-lying excited states.\(^{9,3}\) This alteration gives very good fitting results (Figure 7) with \( g_1 = 2.00, D_{m1} = 0.89 \) cm\(^{-1}\), and \( E_{m1} = 9.5 \times 10^{-2} \) cm\(^{-1}\) for 1, and \( g_2 = 1.99, D_{m2} = -1.58 \) cm\(^{-1}\), and \( E_{m2} = 3.1 \times 10^{-4} \) cm\(^{-1}\) for 2. Other attempts of fitting by using higher values of \( S_T \) are inferior. These fitting results are very informative. \( D_{m2} \) corresponds to an energy barrier \( (U = D_m S_T^2 ) \) for integer spins) of 9.03 K, an almost 2-fold increase in comparison to that of 1 (5.09 K). This large difference in the energy barrier is responsible for the different ac magnetic behaviors. The absence of \( \chi'' \) above 1.8 K in 1 is clearly due to the small energy barrier that can not, on one hand, block the spin reversal caused by \( k_B T \), and on the other hand, stand the “wastage” of the QTM effect as indicated by a relative larger \( E_m \) value.\(^{2,3}\) In contrast, the \( U_{\text{eff}} \) of 2 is almost equal to \( U \), implying that the QTM effect in 2 should be very ineffective. This observation is consistent with the strictly \( C_2 \) symmetry of 2,\(^{2,3}\) which is also confirmed by the very large \( D_m/E_m \) ratio.

**Discussion**

The obtained \( D_m \) values for 1 and 2 are both large in the manganese-based SMMs, suggesting a large axial anisotropy in the two compounds. Accurate evaluation of \( D_m \) requires single-crystal high-frequency EPR (HF-EPR) studies,\(^2\) which, in any case, are also complicated by low-lying excited states.\(^{26}\) In fact, the large \( D_{m2} \) value is consistent with the alignment of 9 JT axes of the Mn\(^{III} \) ions, which all point to the central \( C_3 \) axis with an average angle (denoted as \( \alpha \)), it is an approximate gauge of the angle between the local JT axes and the principal axis of the susceptibility tensor of the molecule\(^{3,26} \) (for details, see Table 2) of 27.5(1)° in 2, a bit smaller than 28.1(1)° (refer to the pseudo-C\(_3\)) axis in 1. In other words, the JT axes in 2 are more parallel to the principal axis of the susceptibility tensor. Such arrangement of the JT axes easily leads to a large negative \( D_m \), which has been
confirmed by the reported Mn2, Mn6, Mn12, Mn21, and Mn30 SMMs with roughly parallel MnIII JT axes. Moreover, the average $D_{i}$ in 2 is probably larger than that in 1 because the MnII octahedra in 2 are more elongated than those in 1 and, consequently, leads to a larger $D_{i}$. The two reasons mentioned above are crucial to the enhancement of the magnetic anisotropy of the Mn15 core in 2, because the vectorial projection of single-ion MnIII anisotropies (octahedral MnIV are fairly isotropic ions) onto the molecular anisotropy axis determines the main magnitude of the molecular $D_{m}$ value. In addition to the above reasons, another source of anisotropy that would affect the whole molecular anisotropy is inter-single-ion dipole–dipole interaction ($D_{ij}$, for details, see Eq S3), which has two different origins, namely through space and through bonding. The former would be very positive for 2 to reinforce the axial anisotropy because all of the Mn15 molecules are arranged in parallel fashion, whereas the opposite result in 1 would be predicted because of the unorderly orientations of the Mn15 molecule. The latter would also be better for 2 because of the more compact arrangement of the Mn15 core, which leads to stronger magnetic exchange interactions. Therefore, a larger axial magnetic anisotropy would be expected in 2 according the above analysis.

4. Conclusion

This work demonstrates the synthesis of a new disklike Mn15 species, and more significantly, the effect of site-specific ligand substitution on the ground-state anisotropy of two Mn15-carboxylate clusters, which may provide a practical way to control the molecular symmetry, tunneling mechanisms, and intermolecular interactions.

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Supporting Information Available: Crystal data (CIF file, additional structural data and plots) and additional magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 2. Angle ($\alpha$) between the JT Direction and the Pseudo- or True-$C_{3}$ Symmetric Axes in 1 and 2

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<th>atom</th>
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<th>atom</th>
<th>$\alpha$ (deg)</th>
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From Pseudo to True $C_{3}$ Symmetry

Inorganic Chemistry, Vol. 46, No. 16, 2007 6443


(19) If one omits the contribution from the dipole–dipole interaction $D_{ij}$, then $D_{m} \approx d_{i} D_{i} \cos^{2}(\alpha)$, where $d_{i}$ is the coefficient related to the coupling scheme one chooses. From this correlation, one can see that the contribution of the larger $D_{m}$ value in 2 is mainly related to three components, namely $d_{i}, D_{i}$, and $\alpha$; for details see Scheme S1, Eq S3, ref 2a, 2c, and 4a.

(20) $D_{ij} \approx J r^{3}$, where $J$ is the coupling constant and $r$ is the distance between the single ions; for details see Eq S3, ref 2a, 2c, and 4.